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Gas phase reaction study of gan in cold wall mocvd reactor by induction heating

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Abstract. Gas reaction of GaN film in cold-wall MOCVD reactor is simulated in this work. The concentration of related substances in various chemical reactions near the cold wall has been analyzed. It is found that when TMGa and NH_3 are separated from the inlet, the reaction occurs first to generate TMGa:NH_3, it is not a dynamic equilibrium reaction, and the next reaction will continue. The GaN concentration distribution is negatively related to the temperature. High temperature enhances the adduct reaction and generates more trimers, and then produce more GaN particles, which have a certain inhibitory effect on the growth of GaN films. Free radicals affect chemical pathways.

1. Introduction

With the development of the information industry, people are increasingly demanding the performance and stability of semiconductor materials [1]. As an important third-generation wide bandgap semiconductor material, GaN has become a key material for the preparation of high-performance electronic devices and high-power blue-violet LEDs with its excellent thermal conductivity and chemical stability [2]. Metal organic chemical vapor deposition (MOCVD) has been widely and maturely used in commercial production as one of the key technologies for the preparation of GaN films [3]. When GaN is grown by MOCVD, the source gases $Ga(CH)_3$ (TMGa) and NH_3 are generally introduced into the MOCVD reaction chamber via the carrier gas H_2 (or N_2). After entering the reaction chamber, the source gas is transported to the substrate surface through a series of complex chemical reactions and physical processes. In order to grow high-quality GaN films, domestic and foreign scholars have made unremitting research on the specific growth process of GaN. Hong Zhang et al. found that chemical kinetic parameters can affect the reaction path [4]. Zhi Zhang et al. calculated that the addition path and the pyrolysis path were affected by the susceptor temperature [5]. Qilong Bao et al. found that the flow of hydrogen can affect the growth of GaN components in AlGaN [6]. These research results are of great significance for guiding the actual growth of GaN films. In this paper, growth simulation of GaN thin films is modeled. The gas phase reaction of GaN thin films grown by cold-wall MOCVD was studied.

2. Reaction chamber model and calculation model

When GaN thin films are grown by MOCVD, the concentration distribution of each reactive gas in the reaction chamber has an important influence on the growth of GaN thin films [7]. Therefore, the analysis of the concentration distribution of various reactants in the reaction chamber is of great

significance. The cold wall MOCVD reaction chamber model of electromagnetic heating is adopted in this paper, as shown in Fig.1(a). Because the reaction chamber is two-dimensional axisymmetric, an axisymmetric model is used to reduce the amount of calculation. In addition, in order to make the simulation results closer to the actual growth, the coupling calculation is adopted to fully consider the interaction between electromagnetic field, thermal field and fluid field. Import gas parameters: TMGa:5sccm, NH_3:30slm, H_2:120slm. The gas phase chemical reactions and related parameters in the reaction process are listed in Table 1.

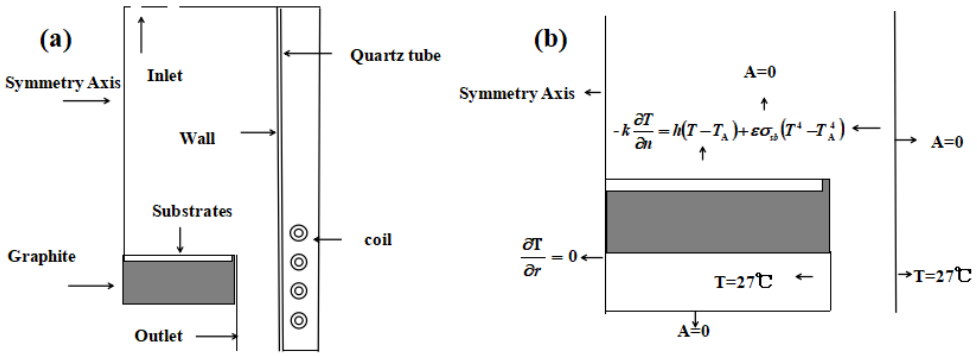

Figure 1. Model of MOCVD reactor(a) and boundary conditions near the substrate(b)

Table 1. Gas-phase chemical reaction

	Gas phase reaction	A	Ea(kcal/mol)	Ref.
G1	TMG→CH_3+DMG	3.5×10^{15}	59.5	[8]
G2	DMG→CH_3+MMG	8.7×10^{7}	35.4	[8]
G3	NH_3+TMG→TMG:NH_3	1.0×10^{9}	0	[9]
G4	TMG:NH_3→NH_3+TMG	9.5×10^{14}	18.5	[9]
G5	TMG:NH_3→CH_4+$DMGNH_2$	1.0×10^{14}	32	[9]
G6	3$DMGNH_2$→[$DMGNH_2$]$_3$	1.0×10^{4}	0	[9]
G7	H_2+CH_3→H+CH_4	2.9×10^{2}	8.71	[9]
G8	H+TMG→CH_4+DMG	5.0×10^{13}	10	[9]
G9	H+DMG→CH_4+MMG	5.0×10^{13}	10	[9]
G10	H+NH_3→H_2+NH_2	5.4×10^{5}	9.91	[10]
G11	NH_3→NH_2+H	2.5×10^{16}	93.7	[10]

The governing equations use the following equations:

The simplified electromagnetic equation is [11]:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial A}{\partial r}\right)+\frac{\partial^2 A}{\partial z^2}=j\mu\omega\sigma A-\mu J_{coil} \tag{1}$$

where ω is angular frequency of the alternating current, μ is magnetic permeability, σ is the electrical conductivity and J_{coil} is the current density applied to the coils.

The two-dimensional heat conduction equation is also solved for the temperature *T*:

$$\rho c_p\frac{\partial T}{\partial t}=\frac{1}{r}\left(\frac{\partial}{\partial r}rk\frac{\partial T}{\partial r}\right)+\frac{\partial}{\partial z}k\frac{\partial T}{\partial z}+Q \tag{2}$$

where ρ is density, c_p is specific heat, *t* is time and *k* is the thermal conductivity. The heat source *Q* is as follows:

$$Q=\frac{\left|J_{eddy}\right|^2}{2\sigma} \tag{3}$$

Where J_{eddy} is the induced eddy current density and

$$J_{eddy} = -j\omega\sigma A + J_{coil} = -\frac{1}{\mu}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial A}{\partial r}\right)+\frac{\partial^2 A}{\partial z^2}\right) \tag{4}$$

The heat, momentum, and mass transfers of the gases in the reactor are governed by four conservation equations that are coupled together: continuity equation[12]:

$$\frac{\partial \rho}{\partial t} + div(\rho U) = 0 \tag{5}$$

Momentum, species conservation and energy equations are generalized into one generic equation[13]:

$$\frac{\partial(\rho\phi)}{\partial t} + div(\rho U\phi) = div(\Gamma_\phi grad\phi) + S_\phi \tag{6}$$

Where div is gradient operator and $div = i\partial/\partial x + j\partial/\partial y + k\partial/\partial z$, ρ density, $U = iu + jv + kw$, $\phi = u, v, w, T$, $\Gamma_\Phi = \eta, k/c_p$ or ρD_{ij}, (k is thermal conductivity, η viscosity, c_p specific heat, D_{ij} binary diffusion coefficient) corresponding to momentum, energy equations or species conservation, respectively. S_ϕ is all other terms in each conservation equation, which is called source term.

The magnetic and heat boundaries condition is shown in Figure.1(b), and the heat boundary condition between the inner walls of the reactor and the outer surfaces of the substrate and the substrate is as follows:

$$-k\frac{\partial T}{\partial n} = h(T - T_A) + \varepsilon\sigma_{sb}\left(T^4 - T_A^4\right) \tag{7}$$

Where n is the unit-normal to the surface, ε is the effective emissivity, σ_{sb} is the Stefan-Bolzman constant, T_A is the temperatures of the walls of the reactor and the substrate, as well as the substrate. h is the heat transfer coefficient. Due to the walls of the reactor is water-cooled during the film growth, the temperature of the surfaces of the reactor is kept at 27°C, and the initial temperature on the system is set to be 27°C. The model is calculated by using VR-Nitride softeware.

3. Analysis of results

We selected five positions to statistical analysis the reaction conditions of each reaction gas in the reaction chamber. Above the substrate, the concentration of each substance on the five parallel line segments of whose distances from the above the substrate are 40mm, 80mm, 120mm, 160mm and 200mm, respectively, so as to study the variation of the gas phase reaction of each substance.The distributions of concentration and temperature of the following substances, which is not special instructions, are at these locations.

3.1. Reaction chamber temperature and pyrolysis reaction

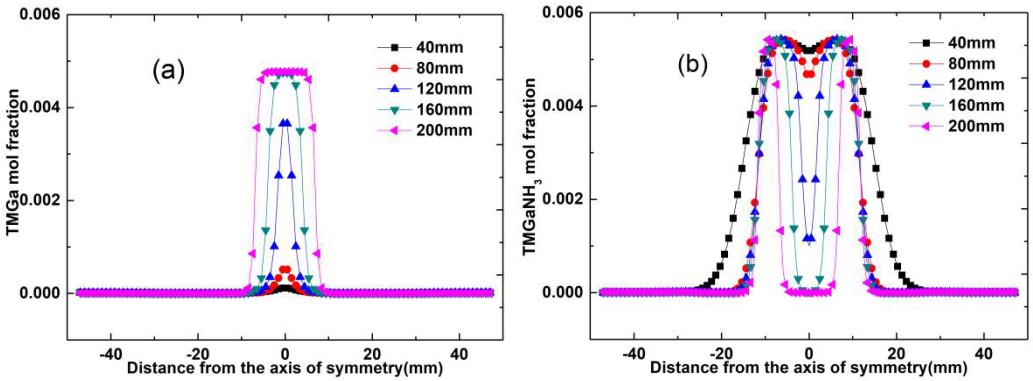

Figure 2. Distributions of TMGa material concentration (a) and TMGa:NH_3 material concentration (b)

Pyrolysis reaction is the main path of GaN growth, and it is of great significance to study the concentration distribution of related substances in pyrolysis reaction. In order to simplify the heating parameters including the current intensity and current frenquency are denoted as A-kHz, for example, 300A and 200kHz are denoted as 300A-200kHz. The following heating parameters are 300A-30khz .

Pyrolysis involves G1, G2, G3, G4. Because reaction G3 does not require activation energy, it occurs at room temperature. As can be seen from Fig.2(a), under the condition of separating the inlet, TMGa at room temperature starts to react rapidly with ammonia gas to generate TMGa:NH_3 after entering the reaction chamber. It can be seen from Fig.2(b), compared with the mass concentrations of TMGa and TMGa:NH_3 at different heights, the TMGa consumed at the same height is basically equal to the molar fraction of the generated TMGa:NH_3, and all TMGa is basically transformed at the distance of 40mm from the substrate.It is shown that G3 and G4 are not dynamic equilibrium reactions, but that all the source reactants have to go through the reaction G3 to continue the next chemical reaction.

3.2. Analysis of reactant concentration changes under different heating temperatures

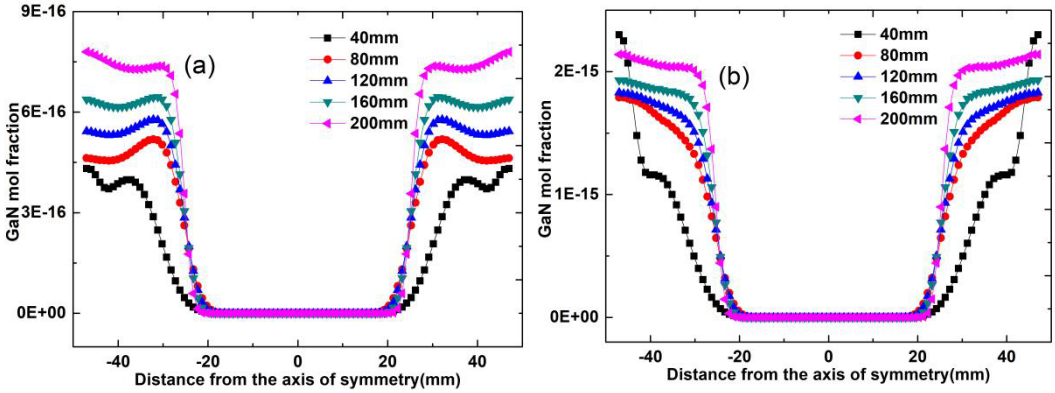

Figure 3. Distributons of GaN under the heating conditions of 300A-30kHz（a）and 350A-30kHz(b)

Fig.3 shows the molar fraction distribution of GaN particle under the heating parmeters: 300A-30kHz (a) and 350A-30kHz (b). It can be seen that the concentration of GaN particles increases with the increasing of temperature. GaN particle is the product of additive path, but the main contribution path of GaN film growth is pyrolysis path. Therefore, the high temperature enhances the adding path, produces more trimer in the reaction chamber, and produces more GaN particles. These large particles could not reach the substrate due to the thermal swimming force, which causes the waste of the source gas. Therefore, high temperature not only causes the waste of source gas, but also inhibits the growth of GaN film.

3.3. Radical reactions

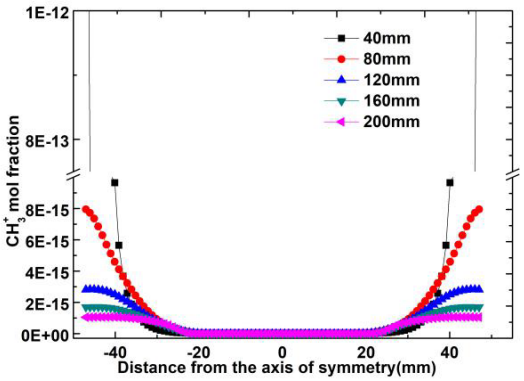

Figure 4. CH_3^+ concentration distributions

Fig.4 shows the distribution curve of the mole fraction of CH_3^+. It can be seen from Fig.4 that the molar fraction of CH_3^+ increases significantly at the height of 40mm from the substrate. It can be found that the content of CH_3^+ in the reaction chamber is concentrated in the region 20mm away from the symmetry axis, which indicates that the generation of CH_3^+ has a significant relationship with the temperature. Moreover, the molar fraction of CH_3^+ is inversely proportional to the heights above the substrate, that is, with the decreased heights, the fraction of CH_3^+ increases, and there is a relatively high concentration of CH_3^+ near the substrate.This indicates that the high temperature promotes the reactions G1 and G2, but the amount of CH_3^+ species is four orders of magnitude smaller than the amount of DMGa and MMGa. On the one hand, it is the reaction that G7 consumes CH_3^+. On the other hand, it is the product H^+ which is the reactant of G8 and G9. This shows that free radical reaction is an important part of gas phase chemical reaction during GaN growth.Free radical affect the chemical reaction path.

4. Conclusion

In this paper, the physical and mathematical model of the cold-wall MOCVD chamber by electromagnetic heating was used to simulate GaN film growth, and its gas phase chemical reaction was investigated. It is found that in the case of pre-separated inlets, all TMGa and NH_3 gas must be converted to TMGa:NH_3 to continue the next reaction. The concentration of GaN particles increases with the increased temperature.Under different heating conditions, compared with the GaN concentration at the same height, the GaN concentration near the substrate changes significantly. High temperature causes the waste of source gas, and inhibits the growth of GaN film. In addition, The chemical reaction path are inflenced by free radical ions such as H^+ and CH_3^+.

Acknowledgments

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References

[1] Ran Zuo, Hong Zhang. III-nitride MOCVD growth in the study of chemical reactions and progress [J].China Light & Lighting,2017(10):4-9(in chinese).
[2] Liang Li, ZhongHui Li , WeiKe Luo, et al. MOCVD homoepitaxial growth of high quality GaN films [J].Journal of Synthetic Crystal,2013,42(05):915-917(in chinese)
[3] Amano H. Development of GaN-based blue LEDs and metalorganic vapor phase epitaxy of GaN and related materials[C]. International Summer School on Crystal Growth. 2016:126-135.
[4] Hong Zhang, Ran Zuo, Zhang G. Effects of reaction-kinetic parameters on modeling reaction pathways in GaN MOVPE growth[J]. Journal of Crystal Growth, 2017, 478:193-204.
[5] Z Zhang, Z Liu, H Fang. Influences of growth parameters on the reaction pathway during GaN synthesis[J]. Journal of Crystal Growth, 2018, 482:44-55.
[6] Bao Q, Zhu T, Zhou N, et al. Effect of hydrogen carrier gas on AlN and AlGaN growth in AMEC Prismo D-Blue ®;, MOCVD platform[J]. Journal of Crystal Growth, 2015, 419:52-56.
[7] XiaoKun He, Ran Zuo. Effect of Addition Reaction on Chemical Reaction Pathways of GaN Grown by MOCVD [J].Journal of Synthetic Crystal,2015,44(12):3687-3691+3698(in chinese).
[8] M.G. Jacko, S.J.W. Price, Can. J. Chem. 41 (1963) 1560.
[9] Baoliang W,Ran Z,Suci M, et al. Quantum Chemistry Study on reaction Paths of GaN /AlN Grown by MOCVD[J].Journal of Crystal Growth, 2015, 44(08):2237-2244.
[10] Jr W C G. Gas-Phase Combustion Chemistry[M]. Springer New York, 2000.
[11] Xiaoxu Zhou , Brian G.Thomas,C.Alberto Hernández B., A.Humberto Castillejos E.,F. Andrés Acosta G. Measuring heat transfer during spray cooling using controlled induction-heating experiments and computational models, Applied Mathematical Modelling 37 (2013) 3181 – 3192.
[12] Ran Zuo, Hong Zhang, Xiang-lin Liu, Transport phenomena in radial flow MOCVD reactor with three concentric vertical inlets, Journal of Crystal Growth,2006,293:498-508.
[13] S.V. Patankar, Numerical Heat Transfer and Fluid Flow, McGraw-Hill, New York, 1980.